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6. AUTHOR(S)
R. Huq, R. Koksbang and G.C. Farrington

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Pennsylvania
Department of Chemistry
Philadelphia, PA 19104-6323

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R. Huq, R. Koksbang, P.E. Tonder and G.C. Farrington

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University of Pennsylvania
Department of Chemistry
Philadelphia, PA 19104-6323

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Electrochemical and Chemical Characteristics of a New Ambient Temperature Li(I) Polymer Electrolyte

Rokeya Huq[1], Rene Koksbang[2], P. E. Tønder[2] and Gregory C. Farrington[1]
[1]Department of Materials Science and Engineering
University of Pennsylvania, Philadelphia, PA 19104
and
[2]Innovision A/S, Energy Research Laboratory (ERL)
Hestehaven 21, DK-5260 Odense S, DENMARK

Abstract

A new type of highly conductive Li^+ polymer electrolyte, referred to as the Innovision polymer electrolyte, is completely amorphous at room temperature and has an ionic conductivity in the range of 10^{-3} S/cm. This paper discusses the electrochemical characteristics (lithium oxidation and reduction), conductivity, and physical properties of Innovision electrolytes containing different dissolved salts. These electrolytes are particularly interesting since they appear to have some of the highest room temperature lithium ion conductivities yet observed among polymer electrolytes.

1. Introduction

Since Armand [1] suggested that solid polymer electrolytes derived from poly(ethylene oxide) (PEO) might be used as electrolytes in thin film, solid electrolyte batteries, major efforts have been made to produce polymer electrolytes with high conductivities at room temperature. The first polymer electrolytes had conductivities of less than 10^{-5} S/cm at 25°C, far too low for use in normal battery applications [2]. Recently, however, electrolyte compositions have been produced which exhibit conductivities competitive with those of non-aqueous liquid electrolytes [3]. These new materials have stimulated major development efforts in polymer electrolyte battery technology.

One of the most successful approaches to increasing the ionic conductivity of polymer electrolytes has been by the addition of various plasticizers. Some of the plasticizers that have been used include polyethylene glycoldimethylether (PEGDME) in PEO (Kelly et al. [4]), which produced an electrolyte with an ionic conductivity of about 10^{-4} S/cm at 40°C, and propylene carbonate in PEO (Munshi [5]). Other plasticizers used include PEG (poly ethylene glycol) and PEGM (glycol dimethyl ether) [6].

More recently, researchers in a joint venture between ERL Laboratories and Mead Corporation have succeeded in preparing a polymer electrolyte composition which combines a conductivity greater than 10^{-3} S/cm at room temperature with good mechanical properties. This new electrolyte has been applied in the development of advanced, thin film polymer electrolyte batteries using Li anodes and V_6O_{13} cathodes. High energy density batteries operating at room temperature with power densities (C/10 and C/2.5 rate) approaching those of NiCd batteries have been demonstrated, according to reports published elsewhere [7].

A great deal of effort has been devoted to the scale-up and commercialization of this new polymer electrolyte technology [8]. Only limited work has been carried out to understand the electrochemical characteristics of the new electrolyte compositions, the factors which influence battery cycle life, or approaches which might be taken to optimize the properties of these new materials. This paper presents the results of a study of the electrochemical characteristics of lithium oxidation and reduction in Innovision electrolytes employing various dissolved lithium salts, for example, $LiClO_4$ and $LiAsF_6$, as well as information regarding their ionic conductivity and general physical properties. Particular attention is focused on the factors that influence lithium electrode cycle life.

The electrolyte discussed in this paper is a radiation-polymerized polyether formed by cross-linking a mixture of acrylate oligomers containing organic plasticizers and dissolved salt. Commonly used plasticizers include propylene carbonate and poly(ethylene glycol dimethylether). Salts include $LiClO_4$, $LiCF_3SO_3$ and $LiAsF_6$. Electrolytes of this type have been described previously in the literature [7-10]. The precise electrolyte compositions used in this are considered proprietary information by Innovision A/S, who supplied samples to the University of Pennsylvania.

2. Experimental Procedures

Electrolytes were prepared by dissolving salts, such as $LiClO_4$ (Chemmetal), $LiCF_3SO_3$ (FC-124, 3M) and $LiAsF_6$ (Electrosalt, Lithco) in two different solvents, propylene carbonate (PC) and poly(ethylene glycol dimethylether) 500 (Poly 500) Hoechst, Germany, and introducing the solutions into the plasticized polyether polymer. Two groups of electrolytes were formed. Composition A refers to compositions incorporating 1M solutions of $LiClO_4$, $LiCF_3SO_3$ and $LiAsF_6$. Composition B consists of electrolytes formed with Poly 500 as the solvent and $LiAsF_6$ and $LiCF_3SO_3$ as the dissolved salts. Electrodes were lithium metal (Johnson Mathey) and a composite electrode consisting of an fine mixture of polymer electrolyte, acetylene black and V_6O_{13}. The preparation and subsequent handling of the materials were carried out inside an Ar-filled dry-box.

Physical characterization included differential scanning calorimetry (DSC), thermogravimetry (TGA) and dynamic mechanical analysis (DMA). Instruments included a DuPont 910 DSC/951 TGA and a DuPont 983 DMA equipped with low mass horizontal clamps designed to test thin or small specimens in a shear mode. The DMA was controlled by a DuPont 2100 Thermal Analyzer. The microstructures of the samples were studied using a Reichert microscope equipped with a Mettler FP5 hot stage.

Polymer film conductivities were measured by complex impedance/admittance analysis from 1 to 10^6Hz. Electrochemical measurements were carried out with a BAS100 electrochemical analyzer (Bioanalytical Systems, Inc.).

For electrochemical studies two different cell configurations were used, (1) a small spring loaded cell with 1 cm^2 area and electrolyte thickness of 2-3 mm, referred to as 'conventional cell' as shown in Figure 1 and (2) a laminate configuration [8] with 16 cm^2 area and electrolyte thickness of 70 μm, referred to as 'thin cell' shown in Figure 2.

3. Results and Discussion

3.1 Differential Scanning Calorimetry

DSC studies and microscopic examination under polarized light [12] shows that the electrolytes of composition A is completely amorphous from about -85° to 100°C. When the material is subjected to several heating cycles there is no evidence that heating-induced crystallization, as has been observed with other polymer electrolyte compositions. However, DSC scans on electrolytes containing Poly 500 [12], composition B, are quite different, the result of differences in the properties of pure Poly 500 and PC. A typical DSC plot for electrolytes of composition B show two Tg's, a small one around -54°C and another around -47°C, and a melting peak around 12°C. Hence composition B is also completely amorphous at room temperature and above but partially crystalline below 12°C.

The chemical stability of the electrolytes of both compositions A and B were determined by DSC analysis of the liquid electrolyte (before radiation) in contact with freshly polished lithium metal. The polymer electrolytes show no evidence of reaction with lithium metal below 182°C, at which point there is a very sharp peak presumably due to the melting of lithium metal. The electrolytes appear stable in the presence of lithium metal up to 180°C, an important characteristic for the battery applications, although it is not possible to

state that similar stability will be observed under extended electrochemical cycling. The composite cathode material containing the polymer electrolyte with PC, acetylene black and V_6O_{13} also appears chemically stable over the temperature range of -90° to 200°C.

3.2 Thermogravimetric Analysis

TGA results show that electrolytes of composition A are much less stable thermally than electrolytes of composition B [12], as can be seen from Table 1. The weight loss at 150°C for composition B is less than 1%, whereas the weight loss of composition A is between 22 to 35%.

TABLE 1

TGA Results

Salt	Plasticizer	% Weight loss at 150 °C
-	pure Poly 500	0.85
$LiCF_3SO_3$	Poly 500	0.8
$LiAsF_6$	Poly 500	0.7
$LiCF_3SO_3$	PC	35
$LiAsF_6$	PC	22
$LiClO_4$	PC	24

3.3 Conductivity Results

As mentioned earlier, electrochemical measurements were carried out with both thin and thick cell configurations. The multi-temperature conductivity results quoted here were measured using a symmetric cell of the type, Li/SPE/Li. Figures 3A and B show a plot of log σ vs 1/T plot from 0°C to 70°C for electrolytes containing $LiAsF_6$ and $LiClO_4$ with PC. There is an obvious curvature below room temperature, but between 30°C to about 80°C a short

region of Arrhenius-type behavior occurs. The activation energy obtained from this temperature range is about 0.28 eV for $LiAsF_6$ and 0.23 eV for $LiClO_4$ with PC. No hysteresis in conductivity is observed upon heating and cooling regardless of the dissolved salt and electrolyte composition. Note also that not only are the room temperature conductivities of these polymer electrolytes high ($2\text{-}3 \times 10^{-3}$ S/cm) but the conductivities remain high even at 0°C (5.5×10^{-4} S/cm and 6.2×10^{-4} S/cm for $LiAsF_6$ and $LiClO_4$ with PC respectively).

Figure 4 shows the log σ vs 1/T plot from 0°C to 60°C for electrolyte of type B containing $LiAsF_6$. The nature of the curve is similar to that observed for electrolytes of type A at room temperature and above, but there is a knee around 12°C corresponding to the crystallization of pure Poly 500, as seen also in DSC results. As in the case of electrolytes of composition A, composition B electrolytes show no hysteresis between heating and cooling and no evidence of a shift in conductivity upon repeated thermal cycling. The activation energy for conduction between 30° and 70°C for electrolytes containing Poly 500 is about 0.39 eV, only slightly higher than the value for composition A .

The room temperature conductivities of the various electrolyte compositions are summarized in Table 2. Electrolytes containing $LiClO_4$ and $LiAsF_6$ with PC have comparable conductivities, about 10^{-3} S/cm, but the conductivity of those containing $LiCF_3SO_3$ with PC is somewhat lower. The use

TABLE 2

Conductivity Results

Salt	Plasticizer	Room Temp. Conductivity (S/cm)
$LiClO_4$	PC	1.89×10^{-3}
$LiAsF_6$	PC	1.61×10^{-3}
$LiCF_3SO_3$	PC	4.83×10^{-4}
$LiAsF_6$	Poly 500	1.94×10^{-4}
$LiCF_3SO_3$	Poly 500	3.68×10^{-5}

of Poly 500 as the plasticizer reduces the conductivity even further, to about 10^{-4} S/cm, for $LiAsF_6$. However, as mentioned earlier, electrolytes

incorporating Poly 500 have superior thermal and mechanical properties [12] and good cyclability characteristics. Electrolytes containing PC tend to be brittle, whereas those with Poly 500 are more rubbery.

AC impedance measurements on a symmetric Li/SPE/Li cell in the frequency range of 0.1 Hz to 10^6 Hz give three well-defined intercepts on the real axis, as shown in Figures 5A and B. Figure 5A shows the whole spectrum, and 5B is an expansion of the high frequency end. The AC impedance results were used to calculate t_+.

3.4 Cyclic Voltammetry

Figures 6A and B show typical CV plots for symmetric Li/SPE/Li cells using a conventional cell and electrolytes containing PC. The scan rate was 20 mV/sec in Figure 6A for a composition containing $LiAsF_6$ and 1 mV/sec in Figure 6B for a composition containing $LiClO_4$. As expected, the faster scan rate gives broader peaks. No difference is observed between CV scans on electrolytes containing different salts but at the same scan rates. The voltage range shown here is ±2.5 V, but other experiments indicate that the electrolytes are stable at least up to ±3.2 V and possibly to ±4.0 V. As Figure 6 shows, the redox process is quite reversible and reproducible. Repetitive scans of up to 30 cycles have been carried out on the same cell without any sign of deterioration or dendrite formation in the case of such a cell.

Figure 7 shows typical CV plots for the electrolyte whose response is shown in Figure 6 but using a thin cell instead of a conventional cell. The composition and the scan rate are the same as in Figure 6B, but the nature of the curve is very different. Although still very reversible, albeit over a smaller voltage range, ± 0.7V in contrast to ± 2.5 V. If the voltage range is extended any further, signs of dendrite formation are observed. This phenomenon is true whether the electrolyte with PC or Poly 500 is studied. As mentioned earlier, the main difference between the two cell configurations is the electrolyte thickness, which was 60-70 μm in the case of the thin cell and 2-3 mm in the case of the conventional cell.

Figure 8 shows a CV recorded on the 24th cycle with a symmetric Li/Li cell of the conventional type using an electrolyte containing Poly 500. The CV is similar to Figure 6A, but the peak separation is larger. Note that even after 23 cycles the cell behaves very reversibly. Cell failure appears ultimately to be the result of dendrite formation, as shown in Figure 9 for the thin cell configuration.

3.5 DC Polarization

Figure 10 shows a typical DC polarization curve at room temperature using lithium electrodes and an electrolyte of composition type B containing

$LiCF_3SO_3$. The current attains a reasonably steady value within the first 15 to 20 minutes and remains steady for the duration of the experiment (3 hrs.). Similar behavior is observed regardless of the electrolyte composition.

3.6 Transport Properties

The transport numbers for Li(I) in the various electrolyte compositions were estimated using both by the AC and DC methods. To calculate t_+ from DC measurements, the method developed by Evan et al. [13] was employed. The initial current was determined from the AC impedance resistance value and the DC voltage applied to polarize the cell. The results obtained by the two techniques at the same temperature are comparable. The transport number, t_+, is temperature dependent as shown in Figure 11 for an electrolyte composition containing $LiClO_4$ and PC. The values upon heating and cooling are comparable and reproducible. An electrolyte composition containing Poly 500 has a temperature dependence of t_+ (not shown here) similar to that observed with PC from room temperature to 70°C. In the case of Poly 500, t_+ is higher at all temperatures than it is with PC.

4. Conclusions

Innovision polymer electrolytes containing propylene carbonate have high room temperature conductivities, of the order of 1.5×10^{-3} S/cm, especially for compositions in which $LiClO_4$ and $LiAsF_6$ are the dissolved salts. Even at 0°C the conductivities are quite high, typically $>5 \times 10^{-4}$ S/cm. Substitution of Poly 500 for PC reduces the room temperature conductivity to the range of 10^{-4} S/cm, but imparts better mechanical, thermal and transport properties to the electrolytes without sacrificing good cyclability.

All of the electrolyte compositions are amorphous at room temperature and show no overt signs of chemical reaction with lithium metal, an important characteristic for battery applications. The electrolytes display good electrochemical and mechanical characteristics over at least 25-30 lithium plating/stripping cycles in cyclic voltammetry experiments.

As might be expected, problems resulting from dendrite formation are more acute for thin cell rather than conventional cells. Ultimate cell failure in either case seem the result of dendrite formation.

5. Acknowledgements

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"Conventional Cell"

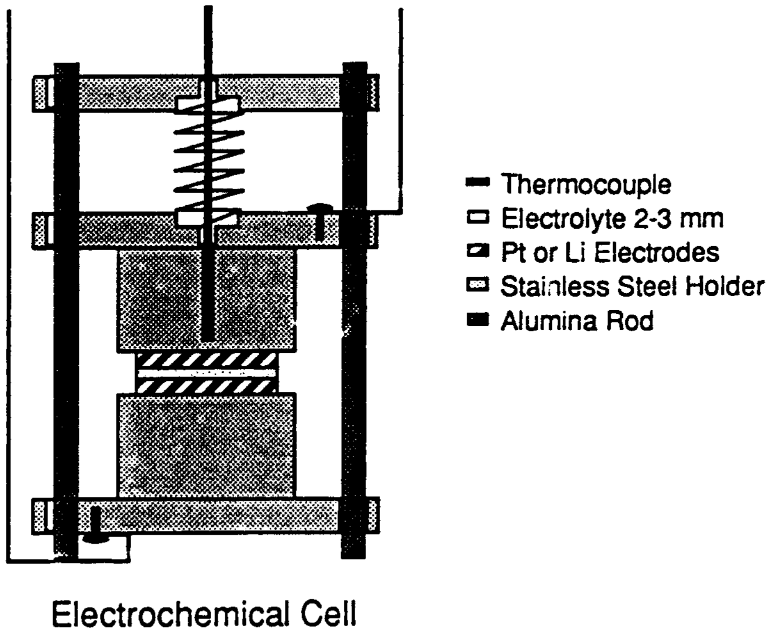

Figure 1. Conventional electrochemical cell.

"Thin Cell"

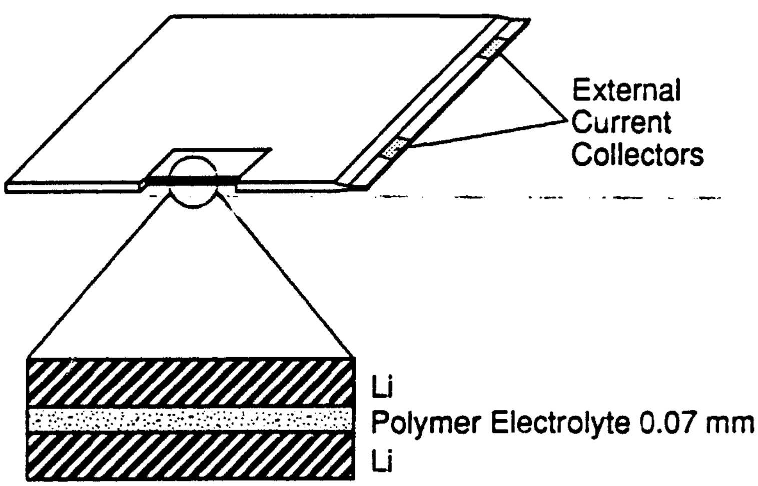

Figure 2. Laminate configuration 'thin cell'.

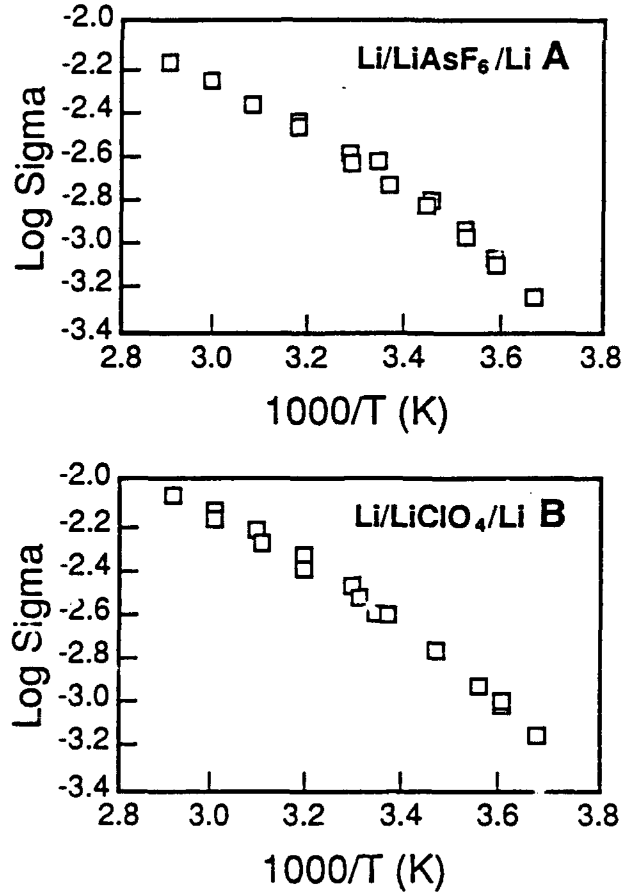

Figure 3. Plot of log σ vs. 1/T from 0°C to 70°C (A) $LiAsF_6$/PC (B) $LiClO_4$/PC.

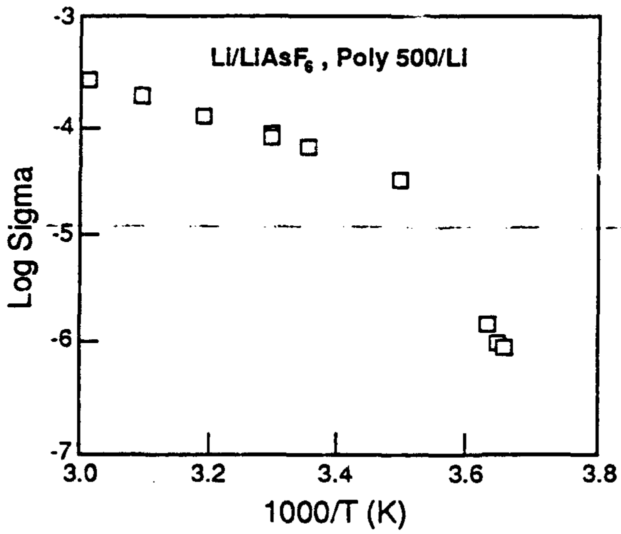

Figure 4. Plot of log σ vs. 1/T from 0°C to 60°C (A) $LiAsF_6$/Poly 500.

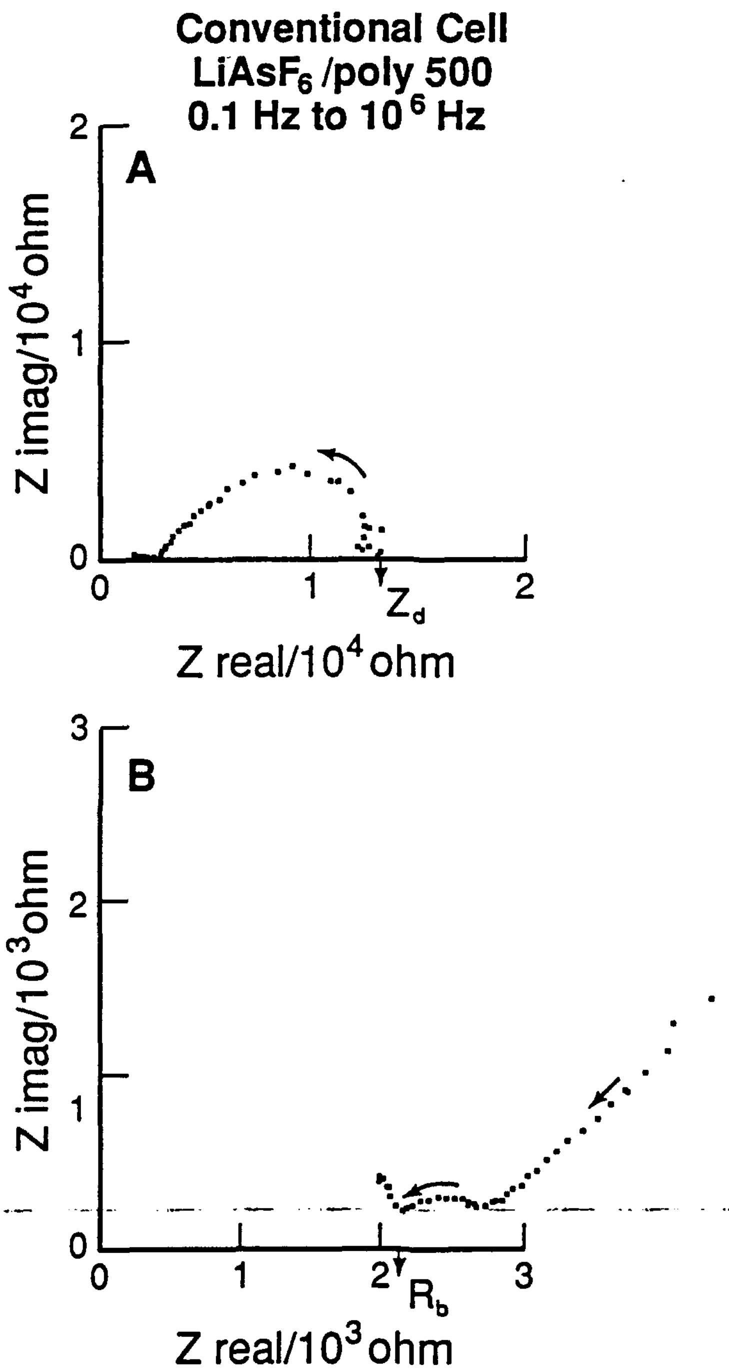

Figure 5. AC impedance spectra of a symmetrical $Li/LiAsF_6$, Poly 500/Li 'conventional cell'.
(A) frequency range of 0.1 Hz to 10^6 Hz
(B) frequency range of 10^2 Hz to 10^6 Hz

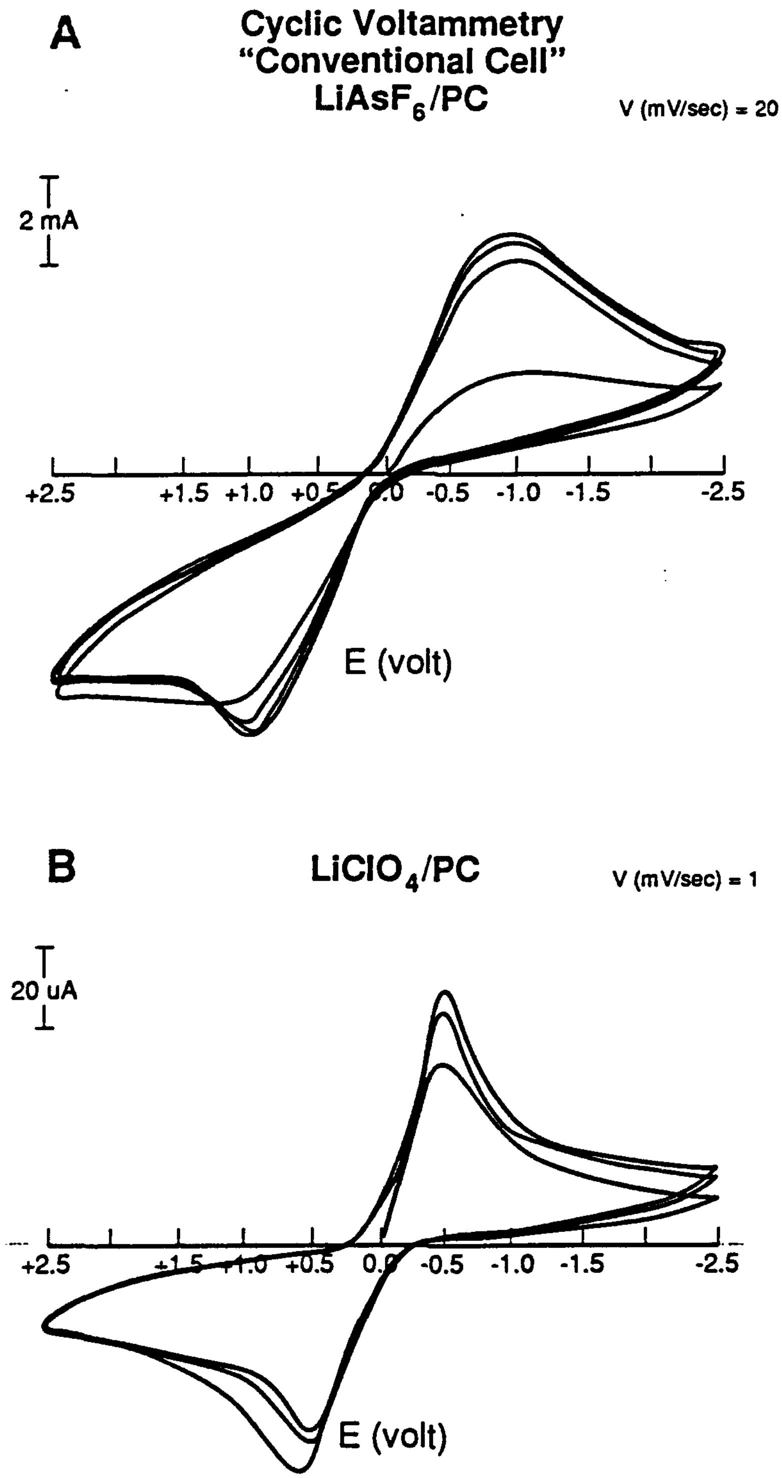

Figure 6. Cyclic voltammogram of Li/SPE/Li 'conventional cell' at room temperature (A) $LiAsF_6$/PC electrolyte at sweep rate of 20mV/sec (B) $LiClO_4$/PC electrolyte at sweep rate of 1 mV/sec.

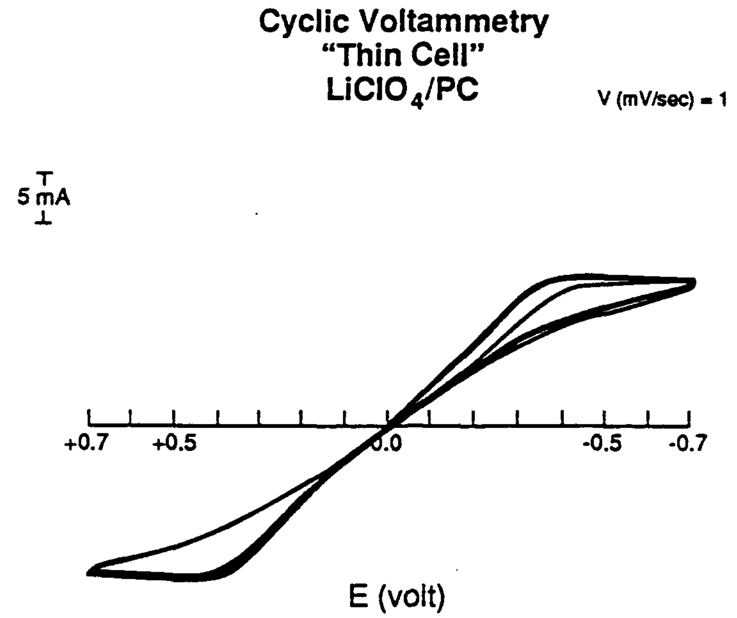

Figure 7. Cyclic voltammogram of $LiClO_4$/PC electrolyte using 'thin cell' at room temperature at sweep rate of 1mV/sec.

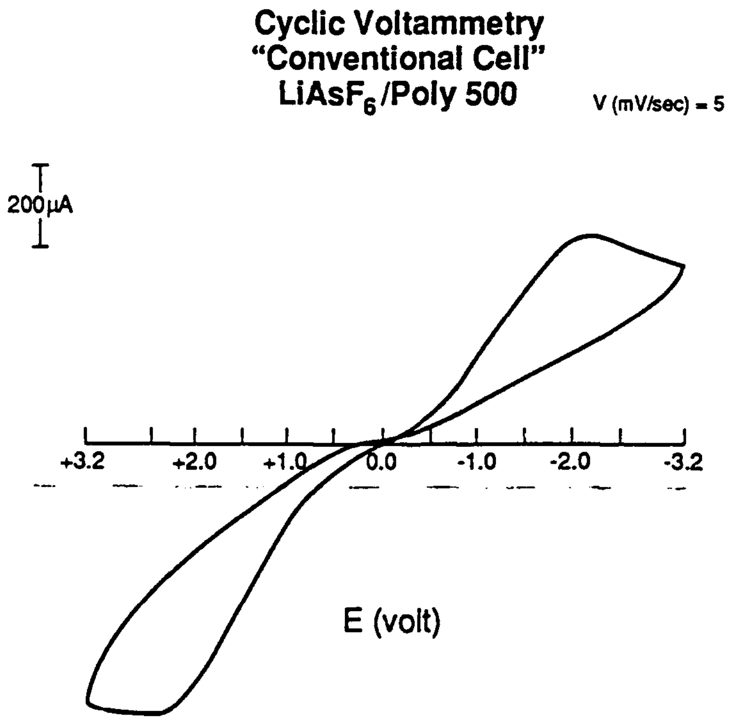

Figure 8. Cyclic voltammogram of the 24th cycle of lithium symmetric cell with $LiAsF_6$/Poly 500 using 'conventional cell' at sweep rate of 5 mV/sec at room temperature.

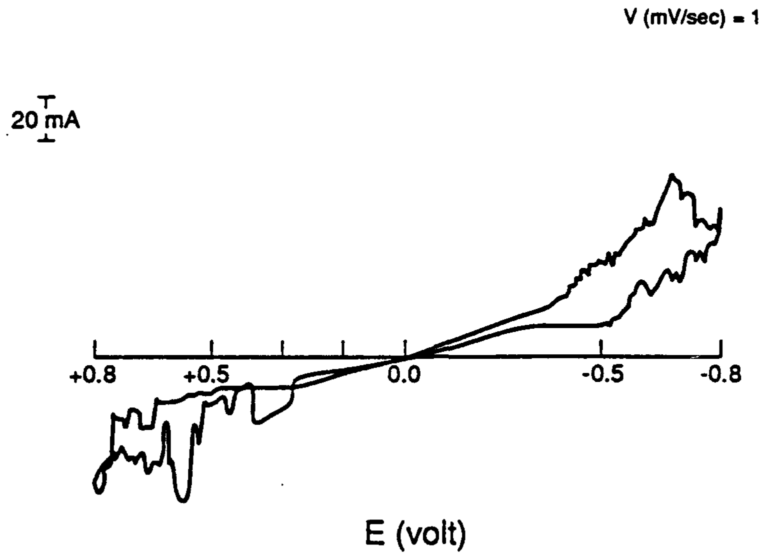

Figure 9. Cyclic voltammogram showing evidence of dentrite formation for 'thin cell' configuration at room temperature.

DC Polarization

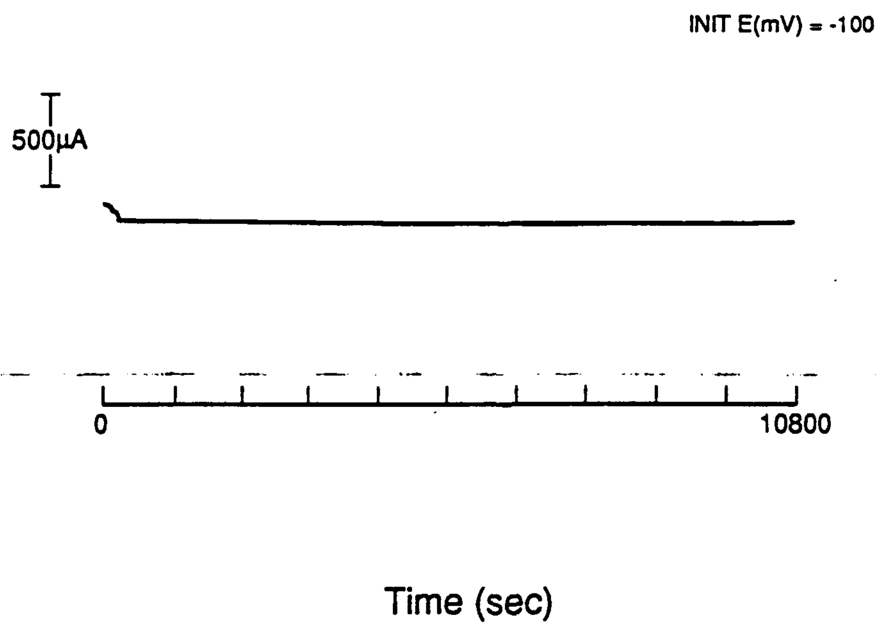

Figure 10. A typical DC polarization curve at room temperature using lithium electrodes.

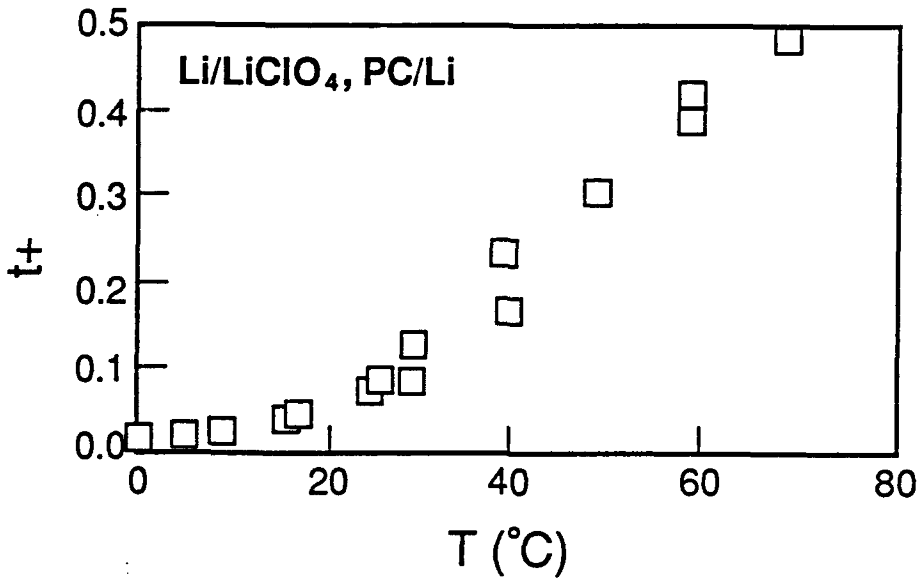

Figure 11. Plot of t+ vs. T °C form 0°C to 70° for $LiClO_4$ with PC using 'conventional cell' configuration.